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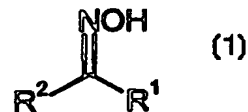
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(21) International Application Number: PCT/US98/17712 (22) International Filing Date: 27 August 1998 (27.08.98) (30) Priority Data: 9718123.4 28 August 1997 (28.08.97) GB (71) Applicant (for all designated States except US): ZENECA INC. [US/US]; 1800 Concord Pike, P.O. Box 15438, Wilmington, DE 19850-5438 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): FERGUSON, Christopher, Allen [US/US]; 1800 Concord Pike, P.O. Box 15438, Wilmington, DE 19850-5438 (US). (74) Agents: FIGG, E., Anthony et al.; Rothwell, Figg, Ernst & Kurz, Columbia Square, Suite 701 East, 555 13th Street N.W., Washington, DC 20004 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

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date**(54) Title:** PROCESS FOR THE EXTRACTION OF METALS FROM AMMONIACAL SOLUTION**(57) Abstract**

A process for the solvent extraction of metals, particularly copper, from aqueous ammoniacal solutions is provided. The extractant is an orthohydroxyarylketoimine of Formula (1), wherein R¹ is a hydrocarbyl group, and R² is an ortho-hydroxyaryl group and the extraction process is carried out in the presence of a kinetic modifier.

Suitable thermodynamic modifiers which can be employed include alkylphenols, alcohols, esters, ethers and polyethers, carbonates, ketones, nitriles, amides, carbamates, sulfoxides, and salts of amines and quaternary ammonium compounds. Preferred orthohydroxyarylketoimines are 5-(C₉ to C₁₄ alkyl)-2-hydroxyacetophenone oximes. Preferred modifiers are highly-branched alkyl esters comprising from 10 to 30 carbon atoms, or highly-branched alkanols comprising from 14 to 30 carbon atoms, or trialkyl phosphates wherein the alkyl groups comprise from 4 to 14 carbon atoms. Extractant compositions comprising a ketoimine and modifier are also provided.



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PROCESS FOR THE EXTRACTION OF METALS FROM AMMONIACAL SOLUTION

The present invention concerns a solvent extraction process and especially a process for the extraction of metals, particularly copper, from aqueous ammoniacal solutions, especially solutions obtained by leaching ores with ammonia.

It is known to extract metals, especially copper, from aqueous solutions containing the metal in the form of, for example, a salt, by contacting the aqueous solution with a solution of a solvent extractant in a water immiscible organic solvent and then separating the solvent phase loaded with metal, i.e. containing at least a part of the metal in the form of a complex. The metal can then be recovered by stripping with solution of lower pH followed for example, by electrowinning. Most commonly, the aqueous metal-containing solutions for extraction are the result of the acid leaching of ores. However it is known that copper can be preferentially leached from certain ores with ammoniacal solutions. This has the advantage that solutions containing especially high concentrations of copper are derived and that there is little contamination of the solution with iron.

Solvent extractants which have found favour in recent years particularly for the recovery of copper from aqueous acidic solutions include oxime reagents, especially o-hydroxyaryloximes. Whilst such reagents have been found to work extremely well in the recovery of copper from acidic solutions, problems have been encountered in the application of such reagents to extraction from ammoniacal solutions. One of these problems results from the high copper concentrations encountered in the ammoniacal solution. This can cause a very high copper loading in the organic solutions, which results in the viscosity of the organic solution increasing to a point where the solution can be difficult to process on an industrial scale. EP-A-0 036 401 solves this problem by the use of an extractant composition comprising two extractants, one being a strong copper extractant, such as an oxime, the other being a weak extractant, a beta-diketone. The use of beta-diketones is also taught by WO 93/04208, where they are the preferred extractant, and the only type to be exemplified.

It has now been found that beta-diketones can suffer from poor chemical stability in the presence of the aqueous ammoniacal leach solution, and therefore rapidly lose their effectiveness and form undesirable impurities. Alternative extractants contemplated by WO 93/04208, orthohydroxyaryl aldioximes, which have proved to be the most effective extractants for copper from acidic solutions, also suffer problems with stability under ammoniacal leach conditions. Furthermore, most extractants are designed for use in acid leach systems, and operate at relatively low pH. WO 93/04208 teaches that employing extractants designed for use with acidic solutions in an ammoniacal system leads to carry over of ammonia into the stripping solution and results in an unacceptable

loss of ammonia from the system. The carry over of ammonia is taught to necessitate the further treatment of the organic phase to remove the loaded ammonia.

Amongst the non-beta-diketone reagents contemplated by WO 93/04208 are three ketoximes, 5-nonyl-2-hydroxyacetophenone oxime, 5-nonyl-2-hydroxybenzophenone oxime and 5-dodecyl-2-hydroxybenzophenone oxime. These reagents are disclosed as being equivalent to aldoximes as less preferred alternatives to the beta-diketones.

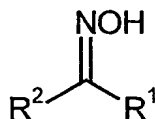
The beta-diketone and oxime extractants contemplated by WO 93/04208 are taught to be soluble to the necessary extent in the water-immiscible solvents commonly employed in solvent extraction. WO 93/04208 discloses that for extractants other than beta-diketones and oximes, a solubility modifier such as an alcohol or ester can be employed where the solubility of the extractant needs to be increased.

During the course of the studies leading to the present invention, it was found that one or more of the problems of poor chemical stability, solution viscosity and ammonia transfer could be ameliorated by the use of a solvent extractant comprising an orthohydroxyarylketoimine and a thermodynamic modifier.

According to a first aspect of the present invention, there is provided a process for the extraction of a metal from ammoniacal solution in which an aqueous ammoniacal solution containing a dissolved metal is contacted with a solvent extraction composition comprising a water immiscible organic solvent and a water-immiscible solvent extractant, whereby at least a fraction of the metal is extracted into the organic solution, characterised in that the solvent extraction composition comprises an orthohydroxyarylketoimine and a thermodynamic modifier.

Metals that may be extracted in the process according to the present invention include copper, cobalt, nickel and zinc, most preferably copper.

The orthohydroxyarylketoimine compounds employed in the present invention are substantially water insoluble and have the formula:



Formula (1)

wherein

R¹ is an optionally substituted hydrocarbyl group

R² is an optionally substituted ortho-hydroxyaryl group,
and salts thereof.

Whilst the invention is described herein with reference to a compound of Formula (1), it is understood that it relates to said compound in any possible tautomeric forms,

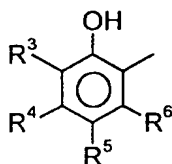
and also the complexes formed between orthohydroxyarylketoximes and metals, particularly copper.

Optionally substituted hydrocarbyl groups which may be represented by R¹ preferably comprise optionally substituted alkyl and aryl groups including combinations of these, such as optionally substituted aralkyl and alkaryl groups.

Examples of optionally substituted alkyl groups which may be represented by R¹ include groups in which the alkyl moieties can contain from 1 to 20, especially from 1 to 4, carbon atoms. A preferred orthohydroxyarylketoxime is one in which R¹ is alkyl, preferably containing up to 20, and especially up to 10, and more preferably up to 3 saturated aliphatic carbon atoms. Most preferably R¹ is a methyl group.

Examples of optionally substituted aryl groups include optionally substituted phenyl groups. When R¹ is an aryl group, it is preferably an unsubstituted phenyl group.

Optionally substituted ortho-hydroxyaryl groups which may be represented by R² include optionally substituted phenols. Examples of optionally substituted phenols which may be represented by R² include those of formula:



wherein R³ to R⁶ each independently represent H or a C₁ to C₂₂, preferably a C₇ to C₁₅, linear or branched alkyl group. Particularly preferably only R⁵ represents a C₁₋₂₂ alkyl group, most preferably a C₇ to C₁₅ alkyl group, with R³, R⁴ and R⁶ representing H.

When R¹ or R² is substituted, the substituent(s) should be such as not to affect adversely the ability of the orthohydroxyarylketoxime to complex with metals, especially copper. Suitable substituents include halogen, nitro, cyano, hydrocarbyl, such as C₁₋₂₀-alkyl, especially C₁₋₁₀-alkyl; hydrocarbyloxy, such as C₁₋₂₀-alkoxy, especially C₁₋₁₀-alkoxy; hydrocarbyloxycarbonyl, such as C₁₋₂₀-alkoxycarbonyl, especially C₁₋₁₀-alkoxycarbonyl; acyl, such as C₁₋₂₀-alkylcarbonyl and arylcarbonyl, especially C₁₋₁₀-alkylcarbonyl and phenylcarbonyl; and acyloxy, such as C₁₋₂₀-alkylcarbonyloxy and arylcarbonyloxy, especially C₁₋₁₀-alkylcarbonyloxy and phenylcarbonyloxy. There may be more than one substituent in which case the substituents may be the same or different.

In many preferred embodiments, the orthohydroxyarylketoxime employed is a 5-(C₈ to C₁₄ alkyl)-2-hydroxyacetophenone oxime, particularly 5-nonyl-2-hydroxyacetophenone oxime.

The composition may comprise one or more different orthohydroxyarylketoximes in which the nature of the substituent groups represented by R¹ and R² differ between component orthohydroxyarylketoximes, especially where the component

orthohydroxyarylketoimes are isomeric. Such isomeric mixtures may have better solubility in organic solvents than a single orthohydroxyarylketoime.

The orthohydroxyarylketoimes are often present in an amount of up to 60% by weight of the composition, commonly no more than 50%, and usually no more than 40 % w/w. Often, the orthohydroxyarylketoime comprises at least 5% by weight, commonly at least 10% by weight and usually at least 20% by weight of composition, and preferably comprises from 25 to 35%, such as about 30%, by weight of the composition.

Thermodynamic modifiers employed in the present invention are substantially water insoluble. Suitable thermodynamic modifiers can be alkylphenols, alcohols, esters, ethers and polyethers, carbonates, ketones, nitriles, amides, carbamates, sulfoxides, and salts of amines and quaternary ammonium compounds.

Alkylphenols which may be used as modifiers in conjunction with the extractant include alkylphenols containing from 3 to 15 alkyl carbon atoms, for example 4-tert-butylphenol, 4-heptylphenol, 5-methyl-4-pentylphenol, 2-chloro-4-nonylphenol, 2-cyano-4-nonylphenol, 4-dodecylphenol, 3-pentadecylphenol and 4-nonylphenol and mixtures thereof. The preferred phenols contain alkyl groups having from 4 to 12 carbon atoms, especially the mixed 4-nonylphenols obtained by condensation of phenol and propylene trimer.

Alcohols which may be used as modifiers in conjunction with the extractant include saturated and unsaturated hydrocarbon alcohols and polyols containing 14 to 30, preferably 15 to 25 carbon atoms. The alcohols are preferably highly branched with the hydroxyl group located approximately midway along the hydrocarbon backbone. Especially preferred are the branched chain alcohols that may be made by condensation of short chain alcohols by the Guerbet process, such alcohols sometimes being referred to as Guerbet alcohols. Optionally, the alcohols may contain an aromatic group or other functional group, particularly an ester group.

Especially useful alcohols may be synthesised from highly branched precursors leading to very highly branched Guerbet alcohols containing a large number of terminal methyl groups. Examples of particularly efficient alcohol modifiers include highly branched isohexadecyl alcohol and iso-octadecyl alcohol, the latter being 2-(1,3,3-trimethylbutyl)-5,7,7-trimethyloctan-1-ol.

Esters which may be used as modifiers in conjunction with the extractant include saturated and unsaturated aliphatic and aromatic-aliphatic esters containing from 10 to 30 carbon atoms. The esters may be mono-esters or polyesters, especially di-esters. The esters are preferably highly branched. Optionally, the esters may contain other functional groups, particularly a hydroxyl group or ether group. Where the ester is a product of the reaction of an alcohol and a mono-carboxylic acid, it is preferred that the alcohol is an alkyl alcohol and comprises from 1 to 6 carbon atoms, and the mono-carboxylic acid comprise from 2 to 16 carbon atoms. Where the ester is a product of the

reaction of an alcohol and a di-carboxylic acid, it is preferred that the alcohol is an alkyl alcohol and comprises from 1 to 6 carbon atoms, and the di-carboxylic acid comprises from 4 to 12 carbon atoms. Where the ester is a product of the reaction of a diol and a mono-carboxylic acid, it is preferred that the diol is an alkyl diol and comprises from up to 6 carbon atoms, and the mono-carboxylic acid comprises from 6 to 16 carbon atoms. Where the ester is a tri-alkyl phosphate, the alkyl groups each commonly comprise from 4 to 14 carbon atoms. Examples of useful esters include isodecyl acetate, methyl decanoate, 2-pentyl octanoate, n-hexyl hexanoate, methyl isooctanoate, 1,4-butanediol dihexanoate, butyl adipate, isobutyl adipate, bis-2-ethoxyethyl adipate, dipropylene glycol dibenzoate, propylene glycol dibenzoate, tributyl phosphate, trioctylphosphate and triethylhexylphosphate, and particularly 2,2,4-trimethyl-1,3-pentanediol isobutyrate and 2,2,4-trimethyl-1,3-pentanediol benzoate.

Ethers which may be used as modifiers in conjunction with the extractant include hydrocarbon ethers and polyethers containing 12 to 30, preferably 15 to 25 carbon atoms. Examples of useful ethers and polyethers include benzyl 2-(2-butoxyethoxy)ethyl ether and benzyl 2-butoxyethyl ether.

Carbonates which may be used as modifiers in conjunction with the extractant include carbonates containing from 4 to 16 carbon atoms. Commonly, the carbonates are alkyl carbonates. Examples of useful carbonates include isobutylcarbonate, isotridecylcarbonate and a carbonate mixture comprising a mixture of C₈ and C₁₀ alkyl groups.

Ketones which may be used as modifiers in conjunction with the extractant include alkyl ketones in which the alkyl group contains from 1 to 20 carbon atoms. Examples of useful ketones include isobutyl heptylketone, diundecyl ketone and 5,8-diethyldodecane-6,7-dione.

Nitriles which may be used as modifiers in conjunction with the extractant include aliphatic and araliphatic hydrocarbonitriles which comprise from 10 to 36 carbon atoms. Examples of useful nitriles include undecylnitrile and oleonitrile.

Amides which may be used as modifiers in conjunction with the extractant include amides containing from 8 to 20 carbon atoms. Amides comprise products which may be derived from the reaction of a primary or secondary amine with a mono- or di carboxylate acid or equivalent, in particular phosgene or equivalents. Examples of useful amides include N,N'-bis-2-ethylhexyl urea, N,N'-bis-2-ethylhexyl 2-ethylhexanamide, N-hexyl 2-ethylhexanamide, N,N'-dibutyl benzamide, N,N'-dibutyl octanamide, N,N'-dimethyl octanamide and N,N'-bis-2-ethylhexyl versatamide.

Carbamates which may be used as modifiers in conjunction with the extractant include alkyl and aryl carbamates. Examples of useful carbamates include N-octyl isotridecylcarbamate and isotridecyl N-tolylcarbamate.

Sulphoxides which may be used as modifiers in conjunction with the extractant include alkyl sulphoxides. An example of a useful sulfoxide is di-2-ethylhexyl sulphoxide.

Salts of amines and quaternary ammonium compounds which may be used as modifiers in conjunction with the extractant include tertiary amines and quaternary ammonium compounds containing alkyl groups having from 8 to 18 carbon atoms and sulphonic acid salts thereof. Examples of sulphonic acids include dinonylnaphthalene sulphonic acid and toluene sulphonic acid.

In the context of the present invention, 'highly branched' as applied to the alcohols and esters means that the ratio of the number of methyl carbon atoms to non-methyl carbon atoms is higher than 1:5 and preferably higher than 1:3.

If desired, mixtures of compounds selected from the group consisting of alkylphenols, alcohols, esters, ethers, polyethers, carbonates, ketones, nitriles, amides, carbamates, sulphoxides, and salts of amines and quaternary ammonium compounds may be employed as modifiers. Particularly preferred are mixtures comprising a first compound selected from the group consisting of alkylphenols, alcohols, esters, ethers, polyethers, carbonates, ketones, nitriles, amides, carbamates, sulphoxides, and salts of amines and quaternary ammonium compounds and a second compound selected from the group consisting of alkanols having from 6 to 18 carbon atoms, an alkyl phenol in which the alkyl group contains from 7 to 12 carbon atoms, and tributylphosphate.

The modifiers often comprise up to 20% w/w of the composition, preferably from 5 to 15 % w/w, and most preferably from 8 to 12% w/w. The weight ratio of modifier to ketoxime is often in the range of from 10:1 to 1:10, commonly from 5:1 to 1:5, and preferably from 1:1 to 1:4.

The aforementioned modifiers may be used in the preparation of extractant compositions containing one or more extractants and one or more modifiers.

Organic solvents which may be used for the extraction include any mobile organic solvent, or mixture of solvents, which is immiscible with water and is inert under the extraction conditions to the other materials present. Examples of suitable solvents include aliphatic, alicyclic and aromatic hydrocarbons and mixtures of any of these as well as chlorinated hydrocarbons such as trichloroethylene, perchloroethylene, trichloroethane and chloroform. Examples of suitable hydrocarbon solvents include low aromatic (<1% w/w) content hydrocarbon solvents such as ESCAID 110 commercially available from Exxon (ESCAID is a trade mark), and ORFOM SX11 commercially available from Phillips Petroleum (ORFOM is a trade mark). Preferred solvents are hydrocarbon solvents including high flash point solvents with a high aromatic content such as SOLVESSO 150 commercially available from Exxon (SOLVESSO is a trade mark) and includes solvents which consist essentially of a mixture of trimethylbenzenes such as AROMASOL H, commercially available from Imperial Chemical Industries PLC (AROMASOL is a trade mark). Especially preferred, however, on grounds of low toxicity

and wide availability are hydrocarbon solvents of relatively low aromatic content such as kerosene, for example ESCAID 100 which is a petroleum distillate comprising 20% aromatics, 56.6% paraffins and 23.4% naphthenes commercially available from Exxon (ESCAID is a trade mark), or ORFOM SX7, commercially available from Phillips Petroleum (ORFOM is a trade mark).

In many embodiments, the composition comprises at least 35%, often at least 45% by weight, preferably from 50 to 70% w/w of water-immiscible hydrocarbon solvent. The composition will comprise at least one orthohydroxyarylketoimine which may be present in an amount up to 54% w/w, and preferably from 25 to 35% w/w. A modifier, particularly an alkylphenol, alcohol or ester modifier may also be present in an amount up to 20%, preferably from 5 to 15%, w/w. Compositions comprising an orthohydroxyarylketoimine which is present in an amount from 25 to 35% w/w and an alkylphenol, alcohol or ester modifier which is present in an amount of from 5 to 15% w/w are particularly preferred.

Particularly preferred solvent extraction compositions are those comprising from 25 to 35% w/w of 5-(C₈ to C₁₄ alkyl)-2-hydroxyacetophenone oxime, 5 to 15% w/w of tridecanol, tributylphosphate, or 2,2,4-trimethyl-1,3-pentanediol isobutyrate or the benzoic acid ester thereof, and from 50 to 70% of water-immiscible hydrocarbon solvent.

The aqueous ammoniacal solution from which metals are extracted by the process of the present invention often has a pH in the range of from 7 to 12, preferably from 8 to 11, and most preferably from 9 to 10. The solution can be derived from the leaching of ores, particularly chalcocite ores, or may be obtained from other sources, for example metal containing waste streams such as from copper etching baths.

The concentration of metal, particularly copper, in the aqueous ammoniacal solution will vary widely depending for example on the source of the solution. Where the solution is derived from the leaching of ores, the metal concentration is often up to 75g/l and most often from 10 to 40g/l. Where the solution is a waste stream, the metal concentrations are often somewhat higher than those from the leaching of ores, for example up to 150g/l, usually from 75 to 130g/l.

The process of the present invention can be carried out by contacting the solvent extractant composition with the aqueous ammoniacal solution. Ambient or elevated temperatures, such as up to 75°C can be employed if desired. Often a temperature in the range of from 15 to 60°C, and preferably from 30 to 50°C, is employed. The aqueous solution and the solvent extractant are usually agitated together to maximise the interfacial areas between the two solutions. The volume ratio of solvent extractant to aqueous solution are commonly in the range of from 20:1 to 1:20, and preferably in the range of from 5:1 to 1:5. In many embodiments, to reduce plant size and to maximise the use of solvent extractant, organic to aqueous volume ratios close to 1:1 are employed, such as 1.5:1 or less, and preferably 1.3:1 or less.

The mole ratio of orthohydroxyarylketoimine to copper transferred is often selected to be in the range of from 2.7:1 to 2:1. Preferably, to achieve improved hydrometallurgical properties, such as reduced viscosity and improved phase disengagement, the mole ratio of oxime to copper transferred is from 2.3:1 to 2.0:1.

5 After contact with the aqueous ammoniacal solution, the metal can be recovered from the solvent extractant by contact with an aqueous strip solution having a pH lower than that from which the metal was extracted.

10 The aqueous lower pH strip solution employed in the process according to the present invention is usually acidic, commonly having a pH of 2 or less, and preferably a pH of 1 or less, for example, a pH in the range of from -1 to 0.5. The strip solution commonly comprises a mineral acid, particularly sulphuric acid, nitric acid or hydrochloric acid. In many embodiments, acid concentrations, particularly for sulphuric acid, in the range of from 130 to 200g/l and preferably from 150 to 180g/l are employed. A low acid concentration but at least 4M chloride containing strip solution as described in European
15 Patent application no. 93301095.1 (publication no. 0 562 709 A2) or International application publication No. WO95/04835 (both of which are incorporated herein by reference) can be employed. When the extracted metal is copper or zinc, preferred strip solutions respectively comprise stripped or spent electrolyte from a copper or zinc electro-winning cell, typically comprising up to 80g/l copper or zinc, often greater than
20 40g/l copper or zinc and preferably from 50 to 70g/l copper or zinc, and up to 200g/l sulphuric acid, often greater than 130g/l sulphuric acid, and preferably from 150 to 180g/l sulphuric acid.

25 The volume ratio of organic solution to aqueous strip solution in the process of the present invention is commonly selected to be such so as to achieve transfer, per litre of strip solution, of up to 50g/l of metal, especially copper into the strip solution from the organic solution. In many industrial copper electrowinning processes often at least 10g/l, preferably from 25 to 35g/l and especially about 30g/l of copper per litre of strip solution is transferred from the organic solution. Volume ratios of organic solution to aqueous solution of from 1:2 to 15:1 and preferably from 1:1 to 10:1, especially less than 3:1 are
30 commonly employed.

A preferred embodiment of the present invention comprises a process for the extraction of a metal from aqueous ammoniacal solution in which:

35 in step 1, a water-immiscible solvent extraction composition comprising a orthohydroxyarylketoimine and a thermodynamic modifier is first contacted with the aqueous ammoniacal solution containing metal,

in step 2, separating the solvent extraction composition containing metal-solvent extractant complex from the aqueous ammoniacal solution;

in step 3, contacting the solvent extraction composition containing metal-solvent extractant complex with an aqueous strip solution of lower pH than the ammoniacal solution to effect the stripping of the copper from the water immiscible phase;

in step 4, separating the metal-depleted solvent extraction composition from the lower pH aqueous solution.

The metal can be recovered from the aqueous strip solution by conventional methods, for example by electrowinning.

The invention is further illustrated, but not limited, by the following examples.

Examples 1 and 2 and Comparison A

A mini-rig trial was carried out to investigate the performance of different solvent extraction compositions in the extraction of copper from a typical ammoniacal copper solution. The process comprised two extraction stages, one wash stage and one strip stage. 500 ml counter-current mixer-settlers stirred at 1000 rpm were employed in each stage. The extraction stages were operated at an organic:aqueous (O:A) ratio of 1.2:1, and the wash and strip stages were operated at an organic:aqueous (O:A) ratio of 1:1. Residence times in each stage were about 3 minutes. The ammoniacal copper solution comprised 30g/l copper, 45g/l ammonia and 75g/l sulphate. The wash solution was a dilute sulphuric acid solution having a pH of 2. The strip solution was an aqueous copper sulphate solution comprising 30g/l copper and 180g/l sulphuric acid. Three different solvent extraction compositions were employed. In Example 1, the extractant comprised 282g/l of 5-nonyl-2-hydroxyacetophenone oxime and 11% w/w 2,2,4-trimethyl-1,3-pentenediol isobutyrate in the hydrocarbon solvent ORFOM™ SX7. In Example 2, the extractant comprised 247g/l of 5-nonyl-2-hydroxyacetophenone oxime and 9.7% w/w 2,2,4-trimethyl-1,3-pentenediol isobutyrate in the hydrocarbon solvent ORFOM™ SX7. In Comparison A, the extractant comprised 282g/l of 5-nonyl-2-hydroxyacetophenone oxime in the hydrocarbon solvent ORFOM™ SX7. During each of the trials, the copper content of the advance electrolyte produced from the strip solution was determined at periodic intervals and used to calculate the percentage copper recovery based on the copper content of the aqueous ammoniacal solution. The percentage copper recoveries achieved were as follows:

Trial	% copper recovery
Example 1	100 (average of 7 determinations)
Example 2	100 (average of 4 determinations)
Comparison A	90.3 (average of 3 determinations)

The results of Examples 1 and 2 clearly demonstrate the improved performance of the process according to the present invention, compared with the results for

Comparison A (not according to the present invention) in which a process omitting the thermodynamic modifier was employed.

Examples 3, 4, 5, 6, 7 and 8, and Comparisons B and C

5 In a separate test, extraction and stripping isotherms were determined for the solvent extraction compositions. In each case, the extractant comprised 118g/l (0.56M) of 5-nonyl-2-hydroxyacetophenone oxime, the Comparison compositions (B and C) had no modifier and the Examples compositions contained 85g/l of modifier chosen from tridecanol (Examples 3 and 6), 2,2,4-trimethyl-1,3-pentanediol isobutyrate (Examples 4
10 and 7) or tributylphosphate (Examples 5 and 8), in the hydrocarbon solvent ORFORM™ SX7.

The loading isotherm was generated using a feed composition comprising 30g/l copper and 45g/l ammonia (2-3g/l free ammonia) at 40°C. This was carried out by contacting the formulated reagent at different organic:aqueous (O:A) ratios, allowing the
15 phases to reach equilibrium and then separating the phases and analysing each phase for metal values. The stripping isotherm was generated by contacting an organic phase loaded with copper with a stripping acid composition comprising 35g/l copper and 150g/l sulphuric acid at 40°C. This was carried out at different organic:aqueous (O:A) ratios, allowing the phases to reach equilibrium and then separating the phases and analysing
20 each phase for metal values. For Examples 3 and 6, the stripping isotherm was measured at O:A ratios of 2:1, 1.5:1, 1:1, 1:2, 1:6, 1:10 and the extract isotherm was measured at O:A ratios of 1:2, 1:3, 1:5, 1:10. For Examples 4 and 7, the stripping isotherm was measured at O:A ratios of 3:1, 2:1, 1.5:1, 1:1, 1:2, 1:4, 1:10 and the extract isotherm was measured at O:A ratios of 1:2, 1:3, 1:10. For Examples 5 and 8, the
25 stripping isotherm was measured at O:A ratios of 2:1, 1.5:1, 1:1, 1:2, 1:5 and the extract isotherm was measured at O:A ratios of 1.5:1, 1:1, 1:1.5, 1:3. For Comparisons B and C, the stripping isotherm was measured at O:A ratios of 3:1, 2:1, 1.5:1, 1:1, 1:1.5, 1:5 and the extract isotherm was measured at O:A ratios of 1.5:1, 1:1, 1:2, 1:3.

30 The expected recoveries were then predicted by iterative means using a McCabe-Thiele construction, utilising the isotherm data generated from the experimental data. The expected recoveries for a 2 extract, 1 strip process at the quoted O:A ratios for extract and strip stages were:

	Modifier	O/A Ratio		% Recovery
		Ext	Strip	
Comparison B	--	1:1	1:1	51.45
Example 3	TDA	1:1	1:1	55.75
5 Example 4	TXIB	1:1	1:1	55.73
Example 5	TBP	1:1	1:1	56.42
Comparison C	--	2.02:1	1:1	96.68
Example 6	TDA	2.17:1	1:1	99.68
Example 7	TXIB	1.97:1	1:1	99.91
10 Example 8	TBP	2.14:1	1:1	98.33

TDA = Tridecanol

TXIB = 2,2,4-Trimethyl-1,3-pentanediol isobutyrate

TBP = Tributylphosphate

15

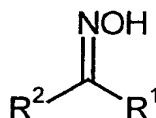
The results clearly demonstrate that improved performance of the process can be achieved according to the present invention, for a range of modifiers, compared with the results for Comparisons B and C (not according to the present invention) in which a process omitting the thermodynamic modifier was employed.

CLAIMS

1. A process for the extraction of a metal from ammoniacal solution in which an aqueous ammoniacal solution containing a dissolved metal is contacted with a solvent extraction composition comprising a water immiscible organic solvent and a water-immiscible solvent extractant, whereby at least a fraction of the metal is extracted into the organic solution, characterised in that the solvent extraction composition comprises an orthohydroxyarylketoxime and a thermodynamic modifier.

2. A process according to claim 1, wherein the metal is copper, zinc, cobalt or nickel, and is preferably copper.

3. A process according to claim 1 or 2, wherein the orthohydroxyarylketoxime is selected from the class of compounds represented by the Formula (1),



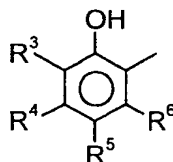
Formula (1)

wherein

R¹ is an optionally substituted hydrocarbyl group, and

R² is an optionally substituted ortho-hydroxyaryl group;
and salts thereof.

4. A process according to claim 3, wherein the orthohydroxyarylketoxime has the general chemical formula:



wherein R³ to R⁶ each independently represent H or a C₁ to C₂₂, preferably a C₇ to C₁₅, linear or branched alkyl group.

5. A process according to claim 4, wherein the orthohydroxyarylketoxime is a 5-(C₉ to C₁₄ alkyl)-2-hydroxyacetophenone oxime, preferably 5-nonyl-2-hydroxyacetophenone oxime.

6. A process according to any preceding claim, wherein the thermodynamic modifier is an alkylphenol, alcohol, ester, ether, polyether, carbonate, ketone, nitrile, amide, carbamate, sulphoxide, or a salt of an amine or quaternary ammonium compound.

5 7. A process according to any of claims 1-5, wherein the thermodynamic modifier is a mixture comprising a first compound selected from the group consisting of alkylphenols, alcohols, esters, ethers, polyethers, carbonates, ketones, nitriles, amides, carbamates, sulphoxides, and salts of amines and quaternary ammonium compounds and a second compound selected from the group consisting of alkanols having from 6 to
10 18 carbon atoms, an alkyl phenol in which the alkyl group contains from 7 to 12 carbon atoms, and tributylphosphate

8. A process according to claim 6 or claim 7, wherein the modifier comprises a
15 highly-branched alkyl ester comprising from 10 to 30 carbon atoms, or a highly-branched alkanol comprising from 14 to 30 carbon atoms, or a trialkyl phosphate wherein the alkyl groups comprise from 4 to 14 carbon atoms.

9. A process for the extraction of copper from ammoniacal solution in which an aqueous ammoniacal solution containing dissolved copper is contacted with a solvent
20 extraction composition comprising a water immiscible organic solvent and a water-immiscible solvent extractant, whereby at least a fraction of the copper is extracted into the organic solution, characterised in that the solvent extraction composition comprises from 25 to 35% w/w of 5-(C₈ to C₁₄ alkyl)-2-hydroxyacetophenone oxime, 5 to 15% w/w of tridecanol, tributylphosphate, or 2,2,4-trimethyl-1,3-pentanediol isobutyrate or the benzoic
25 acid ester thereof, and a water-immiscible hydrocarbon solvent.

10. A solvent extraction composition comprising a water immiscible organic solvent, a water insoluble orthohydroxyarylketoxime and a water insoluble thermodynamic modifier.

30 11. A composition according to Claim 10 wherein the solvent extraction composition comprises from 25 to 35% w/w of 5-(C₈ to C₁₄ alkyl)-2-hydroxyacetophenone oxime, 5 to 15% w/w of tridecanol, tributylphosphate, or 2,2,4-trimethyl-1,3-pentanediol isobutyrate or the benzoic acid ester thereof, and a water-immiscible hydrocarbon solvent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/17712

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C22B 15/00, 19/00, 23/00

US CL :423/24, 99, 139

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/24, 99, 139

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,981,969 A (UITTI) 21 September 1976, cols. 3-4.	1-11
Y	US 4,350,667 A (ANDERSSON et al) 21 September 1982, abstract and cols. 3-4.	1-11
Y	US 5,470,552 A (KORDOSKY et al) 28 November 1995, abstract, claims 1,3,4.	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* "A" "B" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	*T* "X" "Y" *A* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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14 OCTOBER 1998

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29 OCT 1998

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